Application of Laser Polarimetry to the Measurement of Specific Heat Capacity of Molybdenum in the Range 2000 to 2800 K by a Pulse-Heating Technique¹

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¹ Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22-27, 1997, Boulder, Colorado, U.S.A.

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ABSTRACT

Measurement of the specific heat capacity of molybdenum (standard reference material) in the temperature range from 2000 to 2800 K is described. The method is based on rapid resistive self-heating of a rod-shaped specimen from room temperature to the maximum temperature of interest by the passage of a subsecond-duration electrical current pulse through the specimen and on simultaneously measuring the pertinent experimental quantities. The experimental quantities yield: current through the specimen, voltage drop across the specimen, and specimen temperature. The objective of this study is to demonstrate the feasibility of performing accurate thermophysical measurements where the specimen's true temperature is determined from measurements of surface radiance temperature with a pyrometer and normal spectral emissivity with a laser polarimeter. This approach of measuring true temperature eliminates the need of having a blackbody configuration for the specimen. In addition to specific heat capacity, normal spectral emissivity (at 633 nm) and electrical resistivity of molybdenum in the temperature range from 2000 to 2800 K are presented.

KEY WORDS: electrical resistivity; high temperature; laser polarimeter; molybdenum; normal spectral emissivity; pulse heating; subsecond thermophysics.

1. INTRODUCTION

For over 25 years, accurate measurements of several thermophysical properties of solid electrically-conducting materials have been made in our laboratory with a millisecond-resolution pulse-heating technique [1, 2]. The measurements included specific heat capacity of various metals and alloys in the temperature range from 1500 K to the melting point of the specimen. In these experiments, the specimen was in the form of a tube with a small hole fabricated in the wall to approximate blackbody conditions for optical temperature measurements. Because of the tubular geometry, precision fabrication of the specimen has always been difficult and expensive.

Recently, an alternative approach to temperature measurements, that eliminates the requirement for the specimen to have a blackbody configuration, has been considered. In this approach, the specimen is in the form of a solid cylindrical rod and the specimen's true temperature is determined from the measurements of its surface radiance temperature (by spectral radiometry) and its normal spectral emissivity (by laser polarimetry). The validity of the technique has been demonstrated by performing simultaneous measurements, on a tubular specimen, of the normal spectral emissivity by spectral radiometry and laser polarimetry in millisecond-resolution pulse-heating experiments [3].

The objective of the present paper is to establish applicability of the laser polarimetry technique to the determination of the true temperature of a specimen in connection with the measurement of the specific heat capacity of molybdenum. Among the properties that can be measured with the pulse heating technique, specific heat capacity was chosen for the reason that its value is very sensitive to temperature determinations. In pulse heating experiments, specific heat capacity depends not only on temperature but on the derivative of temperature with respect to time. The latter amplifies the effect of

temperature uncertainties on the value of specific heat capacity. Molybdenum was chosen for the reason that it is a Standard Reference Material (SRM) for specific heat capacity as certified by the National Institute of Standards and Technology (NIST) and, as a result, accurate data on this property are available. The results of specific heat capacity on SRM molybdenum over the temperature range from 273 to 2800 K are given in the literature [4]. The high temperature (1500-2800 K) data that had contributed to the establishment of the molybdenum SRM have also been published separately [5].

In this paper, the results of the measurements of specific heat capacity, normal spectral emissivity, and electrical resistivity of molybdenum over the temperature range from 2000 to 2800 K are given and are compared with the pertinent literature values. It should be noted that the results reported here in no way supersede the certified values given earlier [4].

2. MEASUREMENT METHOD

The method is based on rapid resistive self-heating of the specimen from room temperature to high temperatures (up to near its melting point) in less than one second by the passage of an electric current pulse through it; and on measuring, with millisecond resolution, current through the specimen, voltage across the specimen, normal spectral emissivity of the specimen, and radiance temperature of the specimen. The current through the specimen is determined from the measurement of the voltage drop across a standard resistor placed in series with the specimen. The voltage drop across the middle one-third of the specimen is measured between spring-loaded, knife-edge probes. The normal spectral emissivity (at 633 nm) of the specimen is measured with a high-speed laser polarimeter [3]. The surface radiance temperature at 633 nm is determined (by linear interpolation) from measurements of the surface radiance temperatures at two bracketing wavelengths, 624 and 651 nm, with two high-speed

solid-state pyrometers [6,7]. True temperature of the specimen is then determined from the data on radiance temperature and normal spectral emissivity, both corresponding to the same wavelength, using Planck's law. Data are recorded with a digital data acquisition system (16-bit resolution) at the rate of 2 kHz for each experimental quantity. Details regarding construction and operation of the original measurement system, the methods of measuring experimental quantities, and other pertinent information are given in earlier publications [1, 2]. A recent significant modification to the system involving a computer-controlled solid-state switch for the control of the current through the specimen is described elsewhere [8].

3. MEASUREMENTS

The measurements were performed on a rod-shaped molybdenum specimen fabricated from SRM molybdenum stock available at NIST. Spark source mass spectrometry measurements on the original stock have indicated a purity of at least 99.95 mass percent. The details regarding the nature and amount of impurities and other relevant specimen characterizations are documented by the Office of Standard Reference Materials at NIST. The nominal dimensions of the specimen were: length, 76 mm and diameter, 2.4 mm. The specimen was polished to a smooth finish both to provide good reflection characteristics for the laser beam and to minimize radiative heat losses at high temperatures. Before the experiments, the specimen was pulse heated (about 400 ms pulse) three times to about 2000 K to clean its surface of oxides and possible other contaminants.

A total of six experiments were performed. Each experiment provided data in the range 2000 to about 2800 K. The pyrometer operation was optimized for this range by the use of a suitable

neutral-density filter. All the experiments were performed with the specimen in an argon gas (99.999 % pure) environment at slightly above atmospheric pressure.

The specimen was heated from room temperature to about 2800 K in about 400 ms, which corresponds to an average heating rate of about 6.2 K·ms⁻¹. Magnitude of the current pulse through the specimen ranged from about 1440 A at the beginning of the experiment (near room temperature) and 920 A at the end of the experiment (near 2800 K).

A set of eight experimental quantities were recorded with the digital data acquisition system every 0.5 ms throughout the entire pulse heating period. The experimental quantities were as follows: voltage drop across the standard resistor, voltage drop across the middle one-third of the specimen, two pyrometer outputs corresponding to 624 and 651 nm, and four polarimeter outputs. The four polarimeter outputs were used to determine normal spectral emissivity at 633 nm, which is the wavelength of the helium-neon laser of the polarimeter. The two pyrometer outputs yielded radiance temperatures corresponding to wavelengths 624 and 651 nm. These two pyrometer wavelengths bracket the laser wavelength and enable determination (by linear interpolation) of radiance temperature at 633 nm. True temperature was then determined from the measured emissivity and radiance temperature corresponding to the same wavelength (633 nm) for each point. All temperatures reported in this paper are based on the International Temperature Scale of 1990 [9].

4. EXPERIMENTAL RESULTS

4.1. Normal Spectral Emissivity at 633 nm

The method of determining normal spectral emissivity from the four outputs of the polarimeter is described elsewhere [3]. In the present paper, the main reason for determining normal spectral

emissivity was to convert measured radiance temperatures to true temperatures. Since normal spectral emissivity is an important property in its own right, data on emissivity obtained in this work are also reported here. The normal spectral emissivity (at 633 nm) results over the temperature range 2000 to 2800 K for the six experiments are presented in Fig. 1. A linear function was fitted, by the least-squares method, to the emissivity data of all the six experiments. The function (standard deviation 0.003, about 1%) that represents the normal spectral emissivity (at 633 nm) results for molybdenum in the temperature range 2000 to 2800 K is

$$\varepsilon_{\text{n. }633} = 0.4078 - 2.262 \times 10^{-5} \text{T}$$
 (1)

where T is in K. The normal spectral emissivity of molybdenum computed using Eq. (1) is given in Table I. The average normal spectral emissivity at room temperature (295 K) for the six experiments was 0.411 with an average absolute deviation of 0.8% and a maximum absolute deviation of 1.4%.

4.2. Specific Heat Capacity

The details of the procedure for determining specific heat capacity from experimental data have been described in an earlier publication [1]. Specific heat capacity was obtained from measurements of current, voltage, and temperature during the heating period. A correction was applied for the heat loss from the specimen which, at high temperatures, is primarily due to thermal radiation. This correction was obtained from eight auxiliary experiments in the temperature range 1960 to 2840 K. These were brief (about 0.5 s) steady-state experiments which provided data on heat loss from the specimen at a given temperature. This approach has been described in detail in a recent publication [8] in connection with a new technique for measuring hemispherical total emissivity. The heat loss correction amounted to about 1.5% at 2000 K, about 3.5 % at 2500 K, and 5.6 % at 2800 K.

The specific heat capacity results over the temperature range 2000 to 2800 K for the six experiments were fitted, using the least-squares method, by a fourth order polynomial function. The function (standard deviation 0.17, about 0.4%) that represents the specific heat capacity results for molybdenum in the temperature range 2000 to 2800 K is

$$C_p = 6.4790 \times 10^{-2} - 1.1075 \text{ T} + 7.3998 \times 10^{-4} \text{ T}^2 - 2.1791 \times 10^{-7} \text{ T}^3 + 2.4188 \times 10^{-11} \text{ T}^4$$
 (2)

where C_p is in J·mol⁻¹·K⁻¹ and T is in K. The specific heat capacity of molybdenum computed using Eq. (2) is given in Table I. In the computation of specific heat capacity, atomic weight of molybdenum is taken as 95.94 [10]. Figure 2 shows the deviation of the measured specific heat capacity values for the six experiments from the values obtained using Eq. (2).

4.3. Electrical Resistivity

Electrical resistivity was calculated from the relation r = RA/L, where R is the specimen resistance across the voltage probes, L is the distance between the voltage probes, and A is the cross-sectional area of the specimen. A quadratic function was fitted, by the least-squares method, to the electrical resistivity results of the six experiments. The function (standard deviation 0.10, 0.15%) that represents the electrical resistivity results for molybdenum in the temperature range 2000 to 2800 K is

$$\rho = -18.793 + 0.03930 \,\mathrm{T} - 1.7118 \,\mathrm{x} \,10^{-6} \,\mathrm{T}^2 \tag{3}$$

where ρ is in $\mu\Omega$ -cm and T is in K. Electrical resistivity values are based on the room temperature dimensions of the specimen. The electrical resistivity of molybdenum computed using Eq. (3) is given in Table I. Figure 3 shows the deviation of the measured electrical resistivity values for the six experiments from the values obtained using Eq. (3). The room temperature (295 K) value of the

electrical resistivity of molybdenum, as measured with a Kelvin bridge after the pulse experiments, was $5.42 \,\mu\Omega\cdot\text{cm}$.

5. ESTIMATE OF UNCERTAINTIES

The details of estimating the uncertainties in the experimental quantities measured with the present system are given in earlier publications [1,3]. In the present work, the specific items in the uncertainty analysis were recomputed whenever the present conditions differed from those in the earlier publications. The estimated uncertainties (two-standard deviation level) in the experimental quantities and the properties relevant to the present work evaluated at 2400 K (midpoint of the temperature range of the present experiments) are listed in Table II. It can be concluded that the total uncertainty in the properties is not more than $\pm 3\%$ for specific heat capacity, $\pm 1\%$ for electrical resistivity, and $\pm 2\%$ for normal spectral emissivity.

6. DISCUSSION AND CONCLUSION

A comparison of the specific heat capacity of SRM molybdenum measured in the present work (Eq. (2)) with the results on SRM molybdenum reported earlier [5] is shown in Fig. 4 for the range 2000 to 2800 K. It can be seen that agreement is very good: maximum absolute deviation is about 0.5%, with an average absolute deviation of 0.3% over the entire temperature range. Similarly, the results of electrical resistivity of the present work (Eq. (3)) with those obtained earlier [11] on SRM molybdenum show a good agreement in the overlapping temperature range (2000 to 2650 K). The maximum deviation of the present results for electrical resistivity from those of the earlier work is less than -0.7%, with an average absolute deviation of about 0.4% over the entire temperature range.

The earlier measurements [5, 11] were performed on tubular specimens having blackbody configuration, while the present measurements were conducted on rod-shaped specimens. The excellent agreements in both specific heat capacity and electrical resistivity of the present work with the earlier results have demonstrated the reliability of temperature measurements in the present work based on the laser polarimetry technique.

It can be concluded that for accurate measurements of temperature, and hence properties, it may not be essential for the specimen to have a blackbody configuration, and that a simple rod-shaped geometry in conjunction with laser polarimetry can yield accurate property results.

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Table I. Specific Heat Capacity, Electrical Resistivity, and Normal Spectral Emissivity (633 nm) of Molybdenum, According to Eqs. (2), (3), and (1), Respectively.

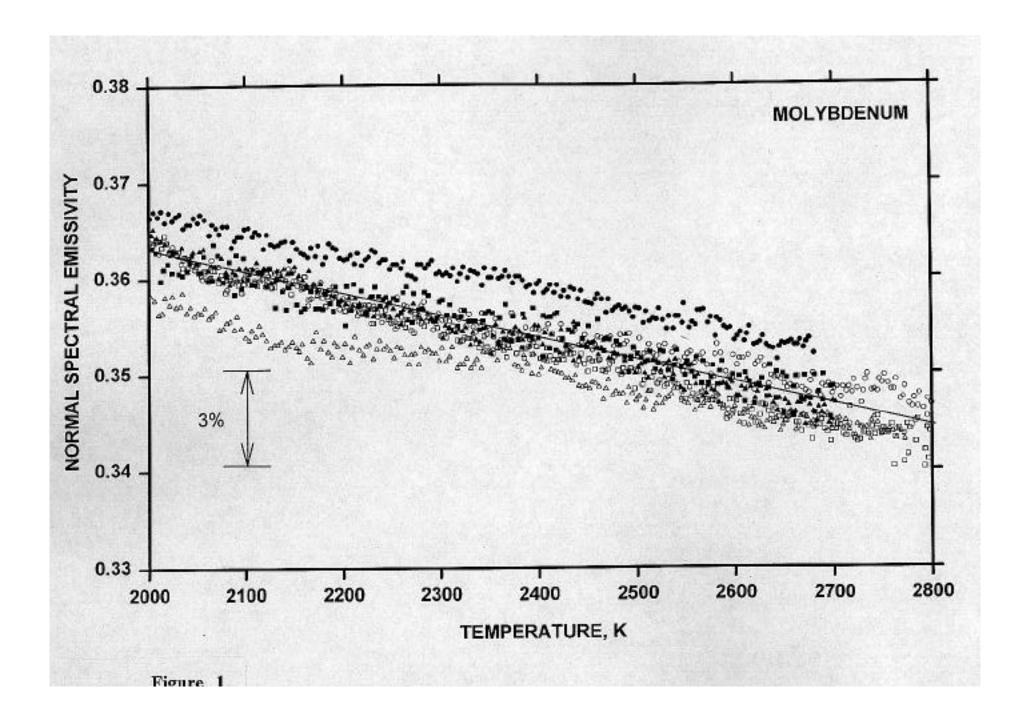
Temperature	Specific heat capacity	Electrical resistivity	Normal spectral emissivity
(K)	$(J \cdot mol^{-1} \cdot K^{-1})$	(mW·cm)	
2000	36.44	52.96	0.363
2100	37.70	56.19	0.360
2200	39.10	59.38	0.358
2300	40.59	62.54	0.356
2400	42.16	65.67	0.353
2500	43.88	68.76	0.351
2600	45.86	71.81	0.349
2700	48.27	74.84	0.347
2800	51.34	77.83	0.344

Table II. Uncertainties (Two-Standard Deviation Level) in the Experimental Quantities and the Resultant Properties

Quantity	Uncertainty (%)
Temperature (radiance)	0.2 (5 K)
Temperature (true)	0.3 (7 K)
Current	0.1
Voltage	0.1
Normal spectral emissivity (at 633 nm	n) 2
Electrical resistivity	1
Specific heat capacity	3

FIGURE CAPTIONS

- Fig. 1. Variation of normal spectral emissivity (at 633 nm) versus temperature for the six experiments on molybdenum. The line represents the fit according to Eq. (1).
- Fig. 2. Deviation of the measured specific heat capacity values for the six experiments on molybdenum from the function expressed by Eq. (2), zero line.
- Fig. 3. Deviation of the measured electrical resistivity values for the six experiments on molybdenum from the function expressed by Eq. (3), zero line.
- Fig. 4. Deviation of the specific heat capacity of the present work (Eq. (2)) from the results of the earlier work [5], (zero line), on molybdenum.



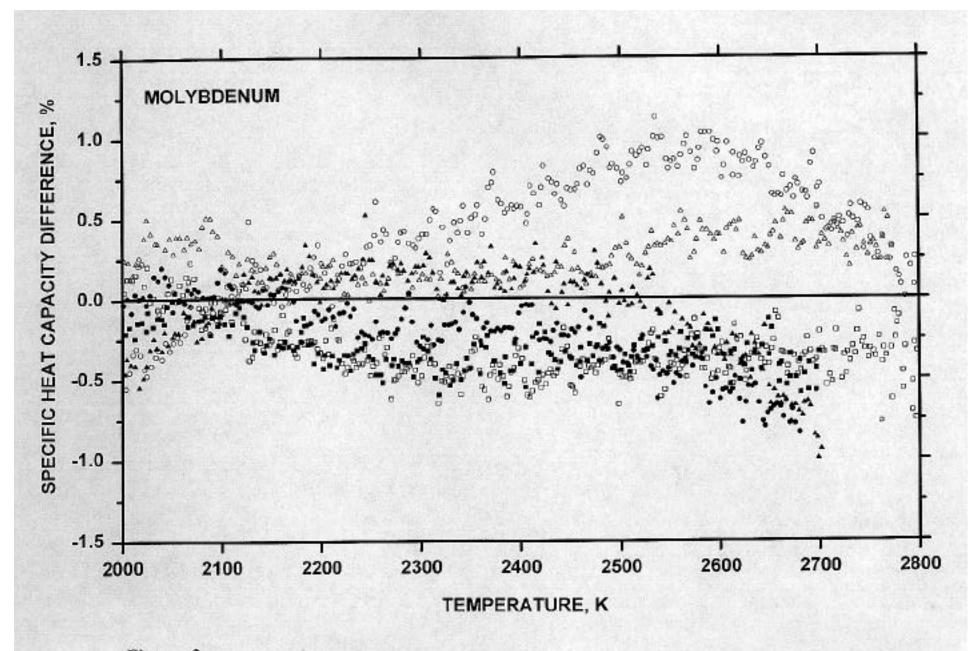
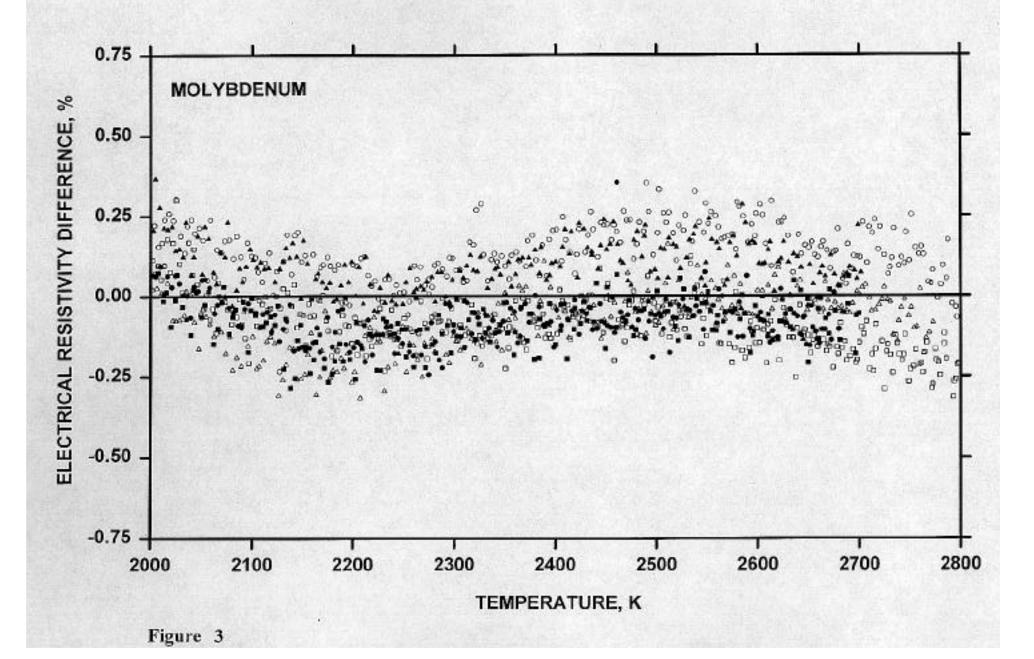


Figure 2



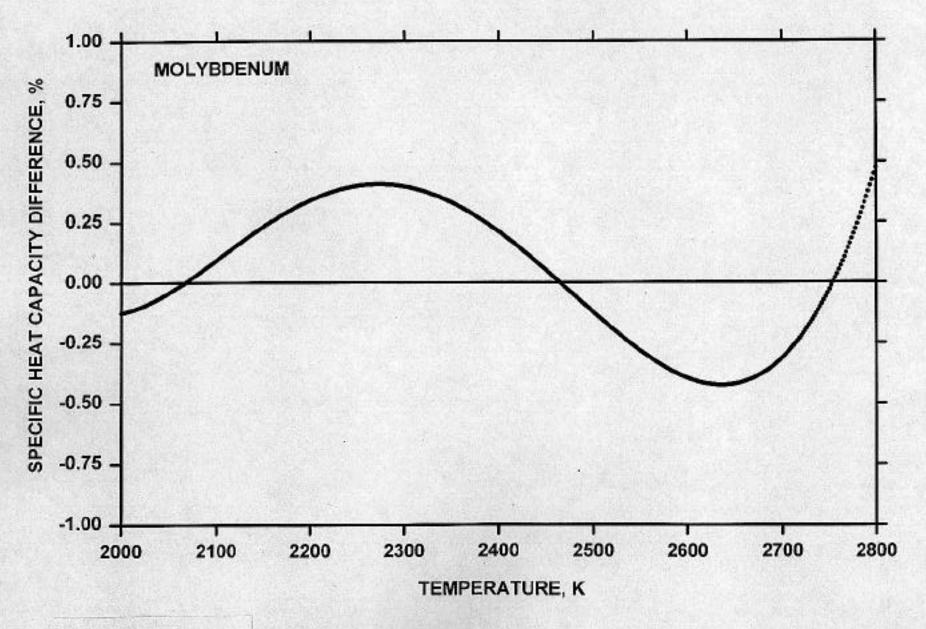


Figure 4